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United States Patent
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Process, for the *desulfurization* of coal

Abstract

A *desulfurization* process for coal ore for the removal of both organic and inorganic (pyritic) sulfurs in coal ore comprises a series of steps including the pulverizing of coal ore; mixing coal particulates with separation reagents, a catalyst and a vehicle; separating the recyclable chemicals and abstracted sulfurs through a select membrane; conditioning the particulates for flotation and sedimentation; clarifying the settleable ash and inorganic sulfurs and the floatable coal from the vehicle; and dewatering the collected coal particulates. The process also provides for regeneration of the catalyst.

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Claims

The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the ***desulfurization*** of coal ore containing both organic and inorganic sulfur, comprising the steps of:

pulverizing coal ore to particle coal size less than 150 microns;

slurrying the particle coal with an effective concentration of abstraction chemicals comprised of at least one reagent for abstracting organic sulfur from the particle coal and water, creating a slurry solution;

mixing and reacting the abstraction chemicals with organic sulfur in the particle coal, such that the organic sulfur is abstracted from the particle coal and released to the slurry solution;

removing the abstracted organic sulfur and recyclable chemicals from the slurry solution by placing the slurry solution in contact with a membrane in a membrane cell through which the abstracted organic sulfur and recyclable chemical passes but through which the particle coal and water does not pass;

transferring the particle coal and water to a conditioner cell and mixing the particle coal and water with an effective concentration of conditioner reagents comprised of reagents for promoting the floatation of the particle coal and for the sedimentation of mineral type compounds in the conditioner cell;

transferring conditioned particle coal and water to at least one clarifying cell and regulating and mixing an effective concentration of frothing agent comprised of at least one chemical for inducing frothing in the clarifying cell;

separating inorganic sulfurs from the particle coal and water by sedimentation;

separating desulfurized particle coal from water by floatation;

transferring desulfurized particle coal to a dewatering device; and

dewatering the desulfurized particle coal and discharging recovered desulfurized coal product.

2. A process for the ***desulfurization*** of coal ore containing organic sulfur comprising the steps of:

pulverizing coal ore to an effective particle coal size;

slurrying the particle coal with an effective concentration of abstraction chemicals comprised of at least one reagent for abstracting organic sulfur from the particle coal and liquid vehicle, creating a slurry solution;

mixing and reacting the abstraction chemicals with organic sulfur in the particle coal, abstracting the organic sulfur from the particle coal and releasing it to the slurry solution;

removing the abstracted organic sulfur and recyclable chemicals from the slurry solution by placing the slurry solution in contact with a membrane in a membrane cell through which the abstracted organic

sulfur and recyclable chemical passes but through which the particle coal and liquid vehicle does not pass;

transferring the particle coal and the liquid vehicle to a dewatering unit; and

separating the liquid vehicle from the desulfurized particle coal and discharging recovered coal product.

3. A process for the **desulfurization** of coal as in claim 2 where the vehicle is water, ethanol, methanol or combinations thereof.
4. A process for the **desulfurization** of coal as in claim 1 or 2 where the abstraction chemicals include a catalyst comprising molybdenum dissolved in a benzene.
5. A process for the **desulfurization** of coal as in claim 1 or 2 where the abstraction chemicals include a hydrogen donator comprising a sodium borohydride prepared by reacting condensed dibromic with tetra alkoxyborate, or a cyanoborohydride, or a combination thereof.
6. A process for the **desulfurization** of coal as in claim 1 or 2 where the membrane cell is a reverse osmosis membrane.
7. A process for the **desulfurization** of coal as in claim 6 where the reverse osmosis membrane comprises a cellulose acetate polymer.
8. A process for the **desulfurization** of coal as in claim 7 where the apparent pore size of the cellulose acetate polymer is about 8 microns.
9. A process for the **desulfurization** of as in claim 1 where the conditioning reagents include pyrogallol, dichlorodimethylsilane and quebracho.
10. A process for the **desulfurization** of coal as in claim 1 where the frothing agent is a combination of eucalyptus oil, cresylic acid and Dow Froth special selection.
11. A process for chemical abstraction of organic sulfur from coal comprising:
 - pulverizing coal ore into particulates;
 - adding water and adjusting the pH to approximately 7.0;
 - adding a water soluble hydrogen donating chemical;
 - adding molybdenum dissolved in a liquid organic matrix selected from the group consisting of aromatic-olefins capable of reversibly reacting with H.sub.2 S; and
 - separating the coal particulates from the water, hydrogen donator, molybdenum and organic matrix.
12. A process as in claim 11 where the organic matrix is benzene.
13. A process as in claim 3 or 10 further comprising the step of regenerating the molybdenum and benzene by purging with a hydrogen source.
14. A process as in claim 11 where the hydrogen donator is a sodium borohydride prepared by reacting

condensed dibromic with tetra alkoxyborate or a cyanoborohydride or a combination thereof.

Description

BACKGROUND OF THE INVENTION

The present invention relates to a process for the **desulfurization** of coal in which the inorganic sulfur (pyrite) and the organic sulfur are removed from treated coal ore.

The dependance on fossil fuels, both in the United States and throughout the world as a source for energy and raw materials has created a demand that has inflated the price of those resources that are easily obtained and easily utilized. Alternate fuels which heretofore have been uneconomical or unfeasible to use as energy or raw material sources would be readily accepted if they could be made compatible with the economic and environmental requirements. Specifically, the use of high sulfur coal would be particularly advantageous if economical processes for reducing the sulfur content could be employed allowing the desulfurized coal to be used in the place of the more expensive naturally occurring low sulfur coals.

The high sulfur coals the bulk of the coal reserves that have been located and identified. As an energy resource, it has been predicted that these known reserves would sustain domestic United States requirements for the next 200 years. At present, commercial exploitation of these reserves is severely limited since the combustion of high sulfur coal results in significant air pollution which typically requires costly abatement procedures for use. Even though abatement procedures can be effective at reducing the sulfur dioxide emissions, none are recognized to be 100 percent effective 100 percent of the time. This situation elevates concerns about the continued use of high sulfur coal products, especially with regard to acid rain.

An alternative to the abatement practices employed in the use of high sulfur coals, is to remove the offending sulfur compounds prior to combustion. An economical and feasible process for achieving this would allow the utilization of coal reserves, largely untapped, thereby reducing dependence on alternate fossil fuels, and at the same time reducing the concerns and chances for environmental pollution. The present invention, as will be seen, achieves the dual goals of efficiency and economy that are required to maximize the utilization of the vast reserves of high sulfur coal.

The inclusion of sulfur in coal occurs in two forms primarily. The first is inorganic, or pyritic, which generally occurs as pyrite, $\text{FeS}_{1.2}$, and associated compounds. The second is organic sulfur, which is sulfur that is linked to the hydrocarbon composition of the coal itself. The distinction between the two forms of coal-related sulfurs is further evidenced in their respective chemical reactivity. The pyritic form undergoes reactions more consistent with ionic salts. The dominance of the iron in the compound also dictates physical characteristics that may be exploited for purposes of separation. The organic sulfurs, on the other hand, exhibit covalent bonding characteristics more like that of organic molecules. Since the desired end product in the **desulfurization** of coal is an organic constituent, physical differences between the organic sulfurs and final product cannot be exploited as easily as in the case of the pyritic sulfurs. Thus, it becomes necessary to utilize other chemical properties of the organic sulfur in order to achieve separation yields of any significance.

The physical removal of the pyritic sulfurs from coal has been achieved by a number of means, both physical and chemical. While some processes for pyritic removal are relevant in terms of feasibility and economy, without the co-removal of organic sulfurs, the ultimate utilization of any such process is

severely limited. However, successful pyritic removal has occurred through the use of floatation, oil-water separation, magnetic separation, and combinations of thermochemical and magnetic processing to name a few. The utilization of these techniques has resulted in a satisfactory result when the interest is in the removal of the pyritic sulfur content exclusively. As mentioned before, this focus results in limitations in applying the technique to all coals since the organic sulfurs are still resident after treatment.

Attempts to liberate the organic sulfurs from coal have included chemical treatment, as would be expected, particularly with carbon disulfide, and also by application of thermal energies to initiate intramolecular liberalization of sulfur. A two-step process for *desulfurization* of organic sulfurs is known where the coal is subjected to an oxidizing environment and then subsequently treated with alkaline solutions. These processes all suffer from the necessary input of resources, either chemical or thermal, that cannot be recovered and otherwise impair the economic feasibility of the *desulfurization* process.

More recently, work has been done utilizing olefins, aldehydes or ketones that effectively react as "sulfur traps" in reactions with organic sulfurs. These reactions occur under pressure which shifts the equilibrium of the trapping reaction towards the sulfurized trapping material. Once the pressure on the separated sulfurized trapping material is reduced and the temperature is elevated, the reaction is reversed to release hydrogen sulfide and regenerate the original trapping reactant. The process takes place under conditions of elevated temperature and pressure and requires batch processing by reactor.

Another recent effort in the removal of organic sulfurs involves the washing of coal particles with an aqueous solution of copper ions. The process proceeds under elevated conditions of temperature and pressure and allows both organic and inorganic sulfurs to be dissolved in the copper solution. After sufficient reaction time has been established, the coal solids are rinsed free of the copper solution thereby separating the solubilized organic and inorganic sulfurs from the remaining coal solids. Both this process and the previously discussed process using olefins, aldehydes and ketones requires the step-wise treatment of coal in reaction vessels. While the recent processes have reduced the cost of chemical inputs, the efficiency is limited by batch type procedures requiring capital intensive equipment.

Despite the obvious incentives for feasible processes for the organic and inorganic *desulfurization* of coal, no one process has been able to demonstrate efficiency and economic feasibility in the continuous production of low sulfur coal products. The present invention achieves such a result in a manner not related to the processes previously known.

SUMMARY OF THE INVENTION

In accordance with the present invention, a process for the *desulfurization* of coal ore containing both organic and inorganic (pyritic) sulfurs, continuously removes the organic and inorganic sulfurs and produces a low sulfur coal of exceptional quality.

In the process of the present invention, coal is initially pulverized preferably to a particle size of 150 microns or less. The coal particulates are combined with abstraction chemicals (a liquid catalyst and separation reagents) and a suspension liquid vehicle (preferably water, alcohol or combination thereof forming a slurry that is mixed and allowed sufficient contact time to react with the organic sulfurs contained in the coal. The catalyzed reaction abstracts organic sulfurs from the coal and releases them to the slurry solution. The slurry solution is then transferred to a membrane cell where the selective porosity of the membrane allows removal of the catalyst and the organic sulfur and remains impermeable to the coal and water.

The coal thus being stripped of its organic sulfur may be treated further for the removal of pyritic sulfurs. The coal and water mixture is transferred to a conditioner where agents inducing flotation and sedimentation are added and allowed to mix. The solution is then transferred to clarifying or sedimentation cells where reaction conditions are monitored and regulated and additional frothing agent is added. Through a series of sedimentation and flotation cells the coal and pyritic materials water are separated, and the pyritic sulfurs are removed.

The separated desulfurized coal particles are transferred to a dewatering device and are recovered as the desulfurized coal product. The clarified water and the recovered catalyst may be returned to the process and hereby recycled.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the process of the present invention.

FIG. 2 is a block diagram showing the pulverizing and sizing process of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention a description for the process of the *desulfurization* of coal ore is described below. The process provides for an effective and unique treatment of high sulfur coals that results in the removal of substantial quantities of organic sulfurs and inorganic sulfurs without the inputting of significant and irretrievable amounts of chemicals or energy.

Coal Sizing

The process commences with the controlled pulverizing of raw coal ore. The actual grinding and pulverizing may be accomplished by conventional equipment already known in the industry. The requirements of the preferred embodiment, however, dictate that some uniformity is established and that limits are placed on the particle size. These requirements are easily met by staging the equipment progressively so that a high degree of confidence is established in the coal sizing as it is outputted from this part of the process.

The crude ore is first screened in the preferred embodiment. Particles that pass through the screening process are less than 150 microns and are immediately routed to a classifier while the bulk of the ore is passed on to the grinder. In the present invention, a dual-rotor breaker is used to perform the bulk of the grinding of the crude ore. The output from the breaker is similarly passed on to a classifier that is calibrated to segregate particles in the 75 micron to 150 micron range. Particles less than 75 microns are treated as fines and are handled in a similar but separate process. The particle sizing is insured by the use of cyclones calibrated at speeds that separate the specified coal particles from particles larger than 150 microns. Thus, a portion of the output from the cyclone is returned to a wet grind process and rerun through the classifier.

By progressively staging the grinding of the coal ore, the particles entering the chemical process are relatively uniform in terms of size and distribution. The maximum efficiency obtained to date in the preferred embodiment is with a preferential particle size of 106 microns. Testing has indicated that when the mode particle size is the indicated 106 microns, that approximately 12% of the particles will range above the 106 micron level up to 150 microns. Essentially no particles above 150 microns are found under these conditions. The lower range of particle size has been fixed at 75 microns for reasons related to equipment characteristics and product handling. Particle sizes less than 75 microns are designated as fines and are optionally side streamed through a parallel treatment process. In this fashion the maximum

throughput of coal particles is insured while provisions are made for the collection of nuisance particles that would otherwise accumulate as dust or waste.

The coal sizing operation is a critical factor in the successful processing of coal for the removal of organic and inorganic sulfurs. The sizing accomplishes two necessary objectives; the first being the release of the mineral or pyritic sulfurs by the physical breaking apart of the coal solids. Numerous processes have employed similar techniques for accessing pyritic sulfurs in coal and the requisite parameters are well known in the industry. The second objective achieved by the pulverizing and sizing process is the increase in the surface area in the remaining coal compounds. This maximizes the access of reagent chemicals to the organic sulfurs. The balance between the particle size and the efficiency of the process is such that decreasing particle size further will not significantly increase the yield of desired low sulfur coal, and conversely increasing the particle size will reduce the efficiency of the chemical processing and result in coal product of predictably higher sulfur content. In some instances, it may be desired in terms of equipment and process utilization to fix the particle size greater than 150 microns. This would be conceivable where the input coal contains sulfur in moderate total amounts or in a proportion between organic and inorganic that allowed the output of coal with acceptable sulfur levels under conditions of reduced organic sulfur removal. It remains, nonetheless, the objective of the present invention to achieve the cleanest coal product possible under practical economic and production restraints.

Organic Sulfur Removal Process

✱ The organic sulfur found in coal ore is covalently bonded to portions of the carbon skeletons found in the various compounds comprising the coal itself. The actual compounds are diverse and are of varying chain lengths. Notwithstanding the diversity and differences in the sulfur compounds, they are dependable and predictable in terms of their reactivity as organic sulfurs. It is this reactivity which allows the sulfur to be selectively abstracted from the coal particles. In the present invention, this reactivity is exploited to abstract and mobilize the sulfur in a form that allows it to be collected and separated from the bulk of the process stream itself.

The first step in abstracting the organic sulfur requires mixing or suspending the coal particulates in water or alcohol or combinations thereof. This may be done on a batch basis, but the preferred embodiment utilizes a continuous flow through system in order to maximize product output. Preferably a cell is made to receive the previously sized particulates of coal by any continuous transfer means, such as a conveyor or pump. The particles thus received are flash mixed under continuous agitation with regulated quantities of water or alcohol. The water added in the present invention is preferably a deionized water which reduces the potential interferences in the reactivity of the process, and as will be discussed momentarily, enhances the efficiency of some of the process components. In the preferred embodiment, water is added to ground coal in the ratio of 9:1, and in the case of alcohols, in the ratio of 9.37:1, weight to weight.

Alcohols may be substituted as a matrix for coal particulate suspension. Typically these would be methanol or ethanol that appear to react and perform as well as the aqueous matrix. The advantages in using water remain chiefly in the low cost, ready availability, and lower volatility.

While the coal particulates and water are being agitated or slurried, the first reagent is added to the cell. This reagent is a hydrogen donating compound, preferably a hydride. The covalent sulfur bonds in organic sulfur compounds can be subjected to hydrogenation and caused to reduce the sulfur and induce it to leave the parent organic compound. Preferably the hydride of choice for this purpose is a modified sodium borohydride prepared by reacting condense dibromic with tetra alkoxyborate, which exhibits a more manageable behavior under the aqueous conditions in the mixing cell. In the alternative, or in

combination, cyanoborohydride may be used with similar ease although with somewhat less efficiency in penetrating the carbon-sulfur bonding. The radicalized organic compound may be reduced totally at the site of the leaving sulfur, thereby consuming the donated hydrogens. In any event, any hydride residue may react with other constituents in the aqueous mix or may be evolved as small amounts of hydrogen gas, the residual hydride having no impairment on the second phase of the chemical treatment.

The addition of sodium borohydride, sodium tetraborohydride or sodium tris-borohydride in the preferred embodiment may occur in any effective concentration up to approximately 8.8 pounds of modified hydride per 10,000 pounds of coal-water suspension. Excess hydride may be added without adverse impairment. The initial reaction readily and spontaneously occurs under ambient conditions and preferably at a pH of 7.0 although reactions are sufficiently propagated throughout the pH range of 6.2 to 8.6. Provisions are made to control pH, since variations in the acid/alkaline balance will alter the rate and efficiency of the hydrogenation reaction. In particular, increasing alkalinity will slow or even stop the reaction.

In addition to the hydride, a second reagent is added to the aqueous mix in order to promote selective separation of the sulfur compounds cleaved from their organic parent compound. This reagent is more properly classified as a catalyst since it is subject to regeneration and recycling within the process. The reagent is comprised of molybdenum in solution in an aromatic olefin. The preferred olefin is benzene in which molybdenum is soluble. The reactions of molybdenum are complex and not totally understood. Molybdenum may exist in a number of valence states, although it is not typically thought to be a strongly ionic species.

In the present invention, the molybdenum solution is added to the mixer cell where it comes in contact with the liberated sulfurs in the aqueous solution. The organic nature of the benzene solvent resists any significant solubility in the aqueous matrix. Under enforced agitation, contact with the constituents of the aqueous matrix is made and the sulfur is thought to be temporarily trapped by its well known tendency to react with olefins. Transfers between the sulfur saturated olefins and the molybdenum takes place spontaneously at room temperature and pressure conditions. This allows the molybdenum disulfide thus generated to act as a convenient transporter of sulfur and retards reversibility in the reaction between sulfur compounds and the organic parents in the coal particles.

In the preferred embodiment, a 52.78% solution of molybdenum in benzene is added to the coal suspension at the rate of 15.2% weight to weight. The reactions initiated by this catalyst occur readily at a pH of 7.0. A total addition of hydride and catalyst compounds of 0.88 pounds per 1,000 pounds of coal suspension has proven effective in pilot runs. Amounts greater than this should not adversely affect coal **desulfurization** other than in economic terms. Lesser amounts may be used depending on the parameters of coal and process, the relationship being determined by the effective amount of catalyst required for abstraction of accessible organic sulfurs.

Upon recycle of the molybdate/benzene solution, an addition of 3.2% of diaryl sulfide is made to retard benzene reactions.

The mixing of both the hydride and catalyst compounds is sufficient after three minutes under most conditions. Individual system characteristics and coal quality may require longer mix periods under certain conditions.

At this stage of the process, the combined slurry is transferred to a membrane cell. The transfer again is preferably continuous and is kept under sufficient velocity or agitation so as to keep the slurry suspended until received by the membrane cell. Preferably, the membrane cell is a flow through type in

keeping with the continuous nature of the present process. The membrane cell also deploys a reverse osmosis membrane at a secondary outlet. The selected membrane allows the permeable transport through the membrane of the reacted molybdenum catalyst including the sulfur. The remaining coal particles and water are not permeable to the membrane, and after retention in the cell for 3.0 to 11.5 minutes, exit for the next step of the process.

The membrane used for the permeable removal of catalyst reagents and sulfur preferably is a cellulose acetate polymer type. This particular membrane has been shown under testing to provide optimal performance in the separation of the desired groups. The typical reverse osmosis membrane requires a driving force to establish a gradient, either physical or chemical, in order to function. In the present case, a slight pressure gradient is developed across the membrane although this gradient is considerably lower than those thought to be required in the past. This unexpected result has been achieved by the recent availability of reduced effective thickness membranes. By employing a membrane of this type, a greater throughput is achieved while still maintaining the desirable aspects of a continuous flow through system.

The pores or passage of the selected reverse osmosis membranes have apparent diameters of 8 microns. The membrane achieves practical transfer characteristics through recently developed techniques that allow extremely thin and selective films to be mated with thicker less selective films. The result is a highly selective membrane with increased transfer properties.

The recyclable chemical and recovered sulfur are collected on the non-process side of the membrane. The liquors may be drawn off continuously or pumped away for storage or as described below, regeneration.

As is the case with typical membrane systems, periodic backwashing is needed to restore the permeability. Since the transmembrane gradient is a lower pressure than would be found in other reverse osmosis applications, the backwash cycle may proceed with a reduced pressure sufficient to overcome the gradient. Membrane life may well be enhanced by this circumstance and actual testing has indicated that four complete cycles can be realized in use. The cycles on the membrane can vary with the kind and quality of the coal being processed, the strength and concentration of the reagents, and the quality of the water. As mentioned before, the deionized water is preferentially used, which in this case reduces loading on the membrane presumably by elimination of the divalent cations found in the average water supply.

The combined catalyst reagents and sulfur separated by the membrane are collected and recycled. The recycling of the molybdenum-benzene solution is accomplished by purging the sulfur from the molybdenum disulfide by hydrogen evolution. The source of the hydrogen may be obtained from many conventional sources such as gas, electrolysis, or hydrogen from dissociated ammonia. The restoration of the molybdenum-benzene solution and the evolution of hydrogen sulfide from the recovered mix allows the molybdenum-benzene solution to be returned to the mixer cell and participate further in the separation of organic sulfur.

Conditioning and Floatation

The coal particulates outputted from the membrane cell have had the organic sulfurs stripped and removed. The remaining inorganic sulfurs as previously discussed exist primarily in the pyritic form which are subject to selective processing for removal as well. In this case, the solution is prepared for the simultaneous floatation of the coal solids and the sedimentation of the pyritic and ash particles. Both floatation and sedimentation of pyritic sulfurs have been used in the processing of coal and are well known in that industry. The advantages of the present invention are such that the results of the organic

sulfur removal process are consistent with subsequent pyritic removal.

The coal particle and water suspension is transferred from the membrane cell into a conditioner cell in this stage of the process. As before, the suspension is transferred under such conditions of velocity and agitation as to maintain homogenous suspensions of the coal while continuously processing the product stream. Once received in the conditioner cell, the suspension is subjected to chemical additions and solution regulation in order to promote the sedimentation of the mineral type compounds. Reagents for promoting floatation of the coal particulates are added as well, the combinations being considered part of the conditioning. The chemicals used in the conditioner cell include the initial reagents pyrogallol, dichlorodimethylsilane, zinc chloride, and methyl or ethyl xanthates in the approximate proportion of 3.11:2.07:0.10:4.71, and are added to the presented suspension at the approximate rate of 2.12 pounds per 100,000 pounds of suspension. The rate of addition may vary since factors such as coal characteristics will affect the conditioning.

Many flotation systems employ tannins in the flotation process. The use of pyrogallol in such applications also is known. The tannins have a marked effect on the wetting properties of aqueous solutions. In particular, it is known that they have an affinity for the pyritic particles suspended in water and will associate with these and similar particles. Pyrogallol also associates with the pyritic particles. This at first induces settling of the pyritic particles but later induces flotation after allowing for periods of standing time. In the continuous process of the present invention, it is beneficial to induce flotation quickly and efficiently by aeration, so that the floating coal particles can be removed before the pyritic particles float.

The introduction of gas bubbles at the beginning of the flotation process allows the small bubbles to be trapped by the coal particles. The buoyancy of the coal is increased, further enhancing the speed and degree of flotation.

In the preferred embodiment, the pyritic materials may be subject to floatation or to precipitation depending on the residence time selected. Experimentation has shown that after admixture for the first three minutes, pyritic materials settle to the bottom, while the coal rises to the surface. They remain effectively separated from the three minute time until about seven minutes, when the pyritic particles rise to the point where admixture commences. After about eleven minutes, all separation is effectively lost. Practical results may be obtained with resident times within the three to seven minute range depending on coal characteristics and process conditions.

Other tannins can be used in place of pyrogallol to achieve essentially the same initial results. A second dosage of a select tannin, quebracho, is used in the present invention to further enhance and accelerate separation, this occurring as a 3% weight to weight ratio of quebracho to suspension. This modified tannin has been shown in testing to accelerate the settling process over that typically seen with pyrogallol alone and exhibits specific effect in concentration ranges of 1.2% to 3.0%.

Compatibly commencing at the same time as flotation is the sedimentation or flocculation of the solids being carried in the suspension. Additions of zinc chloride and methyl or ethyl xanthates are added in order to achieve a coalescence of the remaining particles. While some of the additions of the zinc chloride and xanthates may become included in the final coal product, the expense and physical occurrence are not detrimental to the process. The coalescence of these groups results in product that is less buoyant and precipitates at a faster rate.

Other coalescing agents may be used in much the same manner, especially the class of ionic coagulents or resins, which can be particularly useful. These polymeric resins are well known in the industry, and experience with these compounds indicates that the application of each such individual resin type must

be carefully tested against the particular kind and quality of coal being processed. These resins have individual chemical characters that vary dramatically with the conditions of the colloidal solution or suspension presented. The dosage rates for the xanthates and the polymers are determined for each process by bench top trials.

The use of dichlorodimethylsilane is useful in the preferred embodiment, it is believed, by regulating the surface tension properties of the aqueous solution in order to achieve the optimal bubble sizes for flotation purposes. There also may be other chemical benefits in the use of this product.

The conditioning of the suspension commences with vigorous agitation and variation. The density of the suspension is regulated preferentially to about a 15.2% mix (weight to volume) of coal particles to water. Conditions remain at room temperature and pressures throughout the flotation process. Suspension densities may vary, especially if the average particle size is less than the 106 micron range. Optimal densities for reaction purposes are determined on a case by case basis; however, coal suspensions above 15.2% are difficult to process. The reagents pyrogallol, dichlorodimethylsilane, zinc chloride and the xanthates are mixed and contact is allowed for approximately three minutes. An addition of the quebracho in the preferential amount is made, and the suspension is mixed further for ten seconds.

At this point, the conditioned suspension is transferred to another cell with simultaneous addition of agents designed to induce what is known as frothing. Frothing is considered a necessary step in efficient flotation since it increases the affinity of the coalesced particles for attachment of the bubbles produced by the aeration step. In the present invention, the frothing agents of choice are eucalyptus oil, cresylic acid, and a butylalcohol residue marketed by Dow Chemical Company and known as Dow Froth special selection (Aug. 21, 1987).

The eucalyptus oil is combined with the cresylic acid at a 1:2 ratio. Approximately 1.5 gallons of this solution is added per gallon of Dow Froth and is used as the frothing agent in the preferred embodiment. This combined agent is typically applied at the rate of approximately five gallons per 100,000 gallons of suspension. Effective rates of application may vary as do the other chemical parameters.

After the addition of the frothing agents, the suspension is again continuously transferred to other receiving cells where sedimentation and flotation commence in earnest. In these sedimentation cells additional conditioning or frothing agents may be added as needed in order to replenish chemicals as they are reacted or removed. The suspension is allowed to quiescently traverse through the sedimentation cells, where the coal is collected at the surface and the settleable solids are collected at the bottom of the cells. The actual residence time is dependent on the selection of flotation and settling reagents, the amount of air entrained, the volume of flow and capacity of the cells, and similar criteria. In the present invention, an average settling time of three to seven minutes achieved acceptable results.

The sedimentation and flotation step may be modified by compressing individual process steps such as the addition of conditioning chemicals and frothing agents; however, loss of efficiency can be experienced as a result. Mechanical augmentation may be implemented as a matter of choice through the use of skimmers, flights, or lamella separators. These variations represent advantages that merely serve to shorten the residence time in the sedimentation-flotation phase of the process.

Final Separation and Dewatering

The last stage of the flotation process results in the accumulation of coal solids as coagulated from the aqueous matrix. The solids have now been stripped of both organic and inorganic sulfurs and can be collected continuously for dewatering and transport to final usage. The actual means for removal is well

established in the industry and may consist of collection troughs, scrapers or flights, or merely transfer pumps.

The recovered coal product is thus transported through a dewatering device suitable for separating the small amounts of water that are transported with the coal. In the preferred embodiment the usage of a centrifuge has proved to be most effective. The models manufactured for this purpose by United Coal Company are competent to produce a finished product resulting in approximately 8% moisture content. The water fraction recovered, both by the centrifuge and at the outlet of the final step in the flotation process may be returned to the beginning of the process. This water retains some of the reagents added throughout the steps which typically remain at equilibrium levels low enough that they do not appreciably effect the individual steps. Testing has not yet provided results indicating whether this equilibrium has been fully established for each and every reagent, although repeated recycling has not resulted in any upsets during testing. If required, the expense of wasting the return water completely after four cycles would not be so great as to impair the economic feasibility of the process in any event.

Final Product

The recovery of the finished coal product results in a low sulfur coal that is readily usable in existing applications. Referring to Table 1, the reductions in total sulfur content are approximately 95%. Variations in the amount of sulfur actually removed in the process of the present invention will vary depending on the nature of the coal presented, the parameters set for each phase of the process, the efficiency of the dewatering device among other factors.

A noticeable reduction in ash occurs as well, largely the result of the flotation process. Recovery of coal product is typically high, the losses in output being attributable to the inclusion of coal particulates in ash, the collection of fines in air filters and dust traps, and other portions of the process steps. The losses are not extreme and can be reduced by policing the recovery of fines as previously described within this specification.

TABLE 1

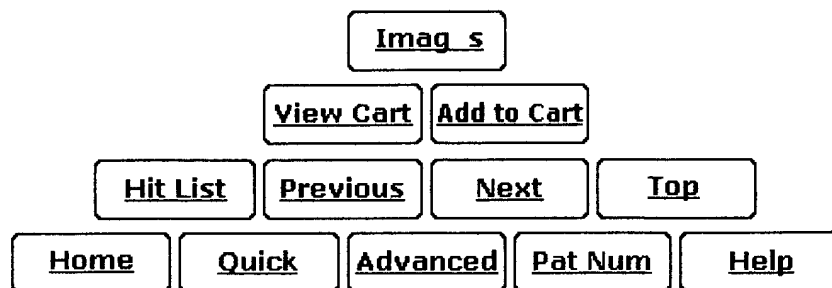
COAL CONSTITUENTS		
	Before Processing	After Processing
ASH	25.0%	5.8%
SULFUR	5.0%	0.25%
MOISTURE	21.0%	8.0%

Those fines that are recovered may be processed through the same steps as herein described. Slight differences allowing for the dynamics of the smaller particles should be made in the rate of additions of the various reagents and in the desired concentration of coal in suspension. Predictably the removal of sulfur from such compounds should occur at a very high rate as an incidence of the increased surface area and penetrability of the reagents. It would be expected that sedimentation and flotation rates may have to be adjusted upwards for time in order to achieve product in the range of 8% moisture content.

From the foregoing, it can be seen that a novel process for the removal of both inorganic and organic sulfurs from coal ore has been described. The advantages of the present invention can be achieved to a greater or lesser extent by slight modifications in the parameters or in the reagents or catalyst described

without departing from the spirit and scope of the invention.

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United States Patent
Davidson**5,238,629**
August 24, 1993

Process of coal *agglomeration***Abstract**

A process for the *agglomeration* of coal fines comprises the steps of mixing the coal fines with an agglomerating liquid which is further comprised of a reagent and a solvent portion. The coal fines are thereafter separated from the agglomerating liquid, dried, and preferentially compressed into pellet form. The process also entails the recovery and return of the agglomerating liquid. The agglomerating liquid of the present invention includes the reagent portion which is a member or a combination of the group consisting of aromatic tertiary amines, nonaromatic cyclic amines or primary organic amines. The solvent is an organic solvent, desirably a member or a combination of the group consisting of toluene, chloroform, carbon disulfide or dimethylacetamide. The pellet formed from the process of the present invention is uniquely water resistant and of controllable hardness.

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Field of Search: 264/109,117,123,37 23/314,313 R
44/550,551,556,593,594,596,599

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Claims

I claim:

1. A process for the **agglomeration** of coal fines comprising the steps of:

slurrying the coal fines with an effective amount of an agglomerating liquid comprising a reagent chemical and a solvent in which the reagent chemical is soluble, creating a slurry solution, the reagent chemical comprising one or a combination of members selected from the group consisting of aromatic tertiary amines, cyclic nonaromatic amines, and primary organic amines;

mixing and reacting the coal fines with the reagent chemical and solvent, such that the coal fines are affected by the reagent chemical and thereafter made amenable to compressible **agglomeration**;

removing the coal fines from the slurry solution;

drying the coal fines by removing the reagent chemical and solvent from the coal fines;

recovering and retaining the reagent chemical and solvent for reuse in the process; and

compressibly agglomerating the coal fines under sufficient pressure to produce **agglomeration**.

2. A process for the **agglomeration** of coal fines as in claim 1, wherein the solvent comprises one or a combination of members selected from the group consisting of toluene, chloroform, carbon disulfide and dimethylacetamide.

3. A process for the **agglomeration** of coal fines as in claim 1, including the step of compressing the dried coal fines into pellet form.
4. A process for the **agglomeration** of coal fines as in claim 1, wherein the coal fines are dried in a pelletizer operable at conditions of sufficient temperature and pressure to evaporate the reagent chemical and solvent.
5. A process according to claim 4, wherein the pelletizer compresses the coal fines at a pressure of no more than about thirty (30) inches Hg at a temperature sufficient to remove unused reagent and solvent by evaporation.
6. A process for the **agglomeration** of coal fines as in claim 1, wherein the reagent comprises quinoline or isoquinoline or a combination thereof.
7. A process for the **agglomeration** of coal fines as in claim 6, including the step of restricting visible light from the slurry solution.
8. A process for the **agglomeration** of coal fines as in claim 1, wherein the agglomerating liquid is admixed in a ratio of agglomerating liquid (milliliters) to coal fines (grams) from about 1:1 to about 2:1.
9. A process for the **agglomeration** of coal fines as in claim 1, wherein said coal fines are derived from sub-bituminous coals and the process includes the step of adding hematite to the coal fines in the amount of approximately one percent (1%) to approximately five percent (5%) by weight of the coal fines.
10. A process for the **agglomeration** of coal fines as in claim 1, including the step of washing the coal fines with ethanol prior to drying.
11. A process according to claim 1, wherein the reagent chemical comprises one or a combination of aromatic tertiary amines selected from the group of consisting of quinoline, isoquinoline, quinoxaline, cinnoline, quinazoline acridine, phenazine, phenanthroline, and phenanthridine.
12. A process according to claim 1, wherein the reagent chemical comprises one or a combination of cyclic nonaromatic amines selected from the group consisting of morpholine, piperazine, piperidine, pyrrolidine, and pyrrole.
13. A process according to claim 1, wherein the reagent chemical comprises one or a combination of primary amines consisting of dipropylamine and triethylamine.
14. A process according to claim 1, wherein the reagent chemical comprises quinoline or isoquinoline or a combination thereof and the solvent comprises dimethylacetamide.
15. A process according claim 1, wherein the reagent chemical and solvent are mixed in the ratio of two (2) parts reagent chemical to about eight (8) parts solvent by volume and the **agglomeration** liquid is admixed with the coal fines in the ratio of about 1:1 (mls liquid to grams of coal fines).
16. A process according to claim 14, wherein the reagent chemical is admixed with coal fines in the ratio of about two-hundredths (0.02) mls to at least two (2) mls reagent chemical to about ten (10) grams of coal fines.
17. A process for the **agglomeration** of coal fines comprising the steps of:

slurrying the coal fines with an effective amount of a reagent chemical and solvent for the reagent chemical, where the reagent chemical is comprised of quinoline or isoquinoline or a combination thereof, and where visible light is substantially eliminated as a condition of the process;

mixing and reacting the coal fines with the reagent chemical and solvent under conditions such that the coal fines are affected by the reagent chemical and thereafter made amenable to compressible **agglomeration**;

removing the coal fines from the slurry solution by settling the coal fines in a sedimentation vessel;

removing the coal fines from the sedimentation vessel;

drying the coal fines by evaporating the reagent chemical and solvent from the coal fines;

recovering and retaining the reagent chemical and solvent from the sedimentation vessel for reuse in the process; and

compressibly agglomerating the coal fines under sufficient pressure to produce **agglomeration**.

18. A process for the **agglomeration** of coal fines as in claim 17, including the step of recovering and retaining the reagent chemical and solvent evaporated from the coal fines.

19. A process for the **agglomeration** of coal fines comprising the steps of:

slurrying the coal fines with an effective amount of an agglomerating liquid comprising n-xylene and pyridine, creating a slurry solution;

mixing and reacting the coal fines with the agglomerating liquid in the presence of an effective amount of the solvent toluene, such that the coal fines are affected by the agglomerating liquid and thereafter made amenable to compressible **agglomeration**;

removing the coal fines from the slurry solution;

drying the coal fines by removing the agglomerating liquid and solvent from the coal fines;

recovering and retaining the agglomerating liquid and solvent for reuse in the process; and

compressibly agglomerating the coal fines under sufficient pressure to produce **agglomeration**.

Description

BACKGROUND OF THE INVENTION

The present invention relates to the field of coal processing. More specifically, the invention relates to the recovery of coal fines which are traditionally regarded as waste by-products of various coal processes or coal handling.

The generation of coal fines during the processing of coals and while coal products are being transported

has long been an industry problem. The tendency for coal and related products to randomly fracture into particles has never been successfully regulated such that grinding processes result in a wide distribution of particle sizes. Similarly, the transport or handling of coals has the effect of inducing contact between larger pieces and results in the creation of fines.

The typical methods for handling these fines usually depend on systems customized for coal fines. Thus in those facilities where fines are being generated routinely, many are handled through slurry or hopper systems and are directed to settling ponds. The accumulations in these ponds are dealt with en masse. In the transport of coals, the fines will fall to the bottom of the transport container. In cases such as ship transport, the level of fines accumulating in the bottom of the hold can lead to conditions where spontaneous combustion can take place. This feature of waterborne shipments of coal has led to sensitivity in the duration of shipments and as to the type and design of the vessel carrying the coal.

Recognition of the value of coal fines as an energy and chemical resource is long standing. The difficulty to date has been the poor economics involved in reprocessing the fines to a usable state or the lack of compatible and consistent outlets for coal fine consumption. The present invention has been successful in producing a usable coal product from coal fines while maintaining an economic advantage.

Other processes are known where coal fines are subjected to various conditions, typically high heats and/or pressure, and then are mechanically compressed or formed into pellets or briquettes. These processes are suited to low throughputs or batch operations and have energy or equipment requirements that make them unattractive for most of the situations described above.

One process is known where the coal fines are subjected to solvents that cause a partial and selective organic extraction to occur. The coal fines used in this process are preferentially those with paraffin content such that the relatively sticky compounds trapped in the coal matrix are brought to the surface of the coal particles. In this manner the particles are made to stick to each other and create clusters or clumps. Obvious drawbacks to this process include the required restriction of applying the solvents to certain coals. Most coal fines generated would not possess the requisite constituents for this process.

A need for a low cost method for the recovery and handling of coal fines has remained until the development of the present invention. As such it is at least one object of the present invention to provide a method for agglomerating coal fines as generated from many different sources. In addition, the method has significant economic advantages over past attempts in this field in that little energy input is required and much of the process chemistry is recycled.

SUMMARY OF THE INVENTION

A process for the **agglomeration** of coal fines comprises collecting coal fines of appropriate size, slurrying the coal fines with **agglomeration** reagents and solvents, and then separating and pelletizing reacted coal fines, thereby removing reagent liquor from the fines.

Specifically, coal fines with particulate size less than two hundred (200) microns are selected for treatment. They are subjected to sufficient mixing and contact with the **agglomeration** reagents so as to cause the desired result. The reagent liquor is comprised of reagent and solvent fractions, such that there is a 1:1 ratio generally of liquor to coal fines (milliliters to grams). The slurry thus created is utilized as vehicle for handling and reacting with the coal fines, with a small portion of the reagent being incorporated into the agglomerated coal product.

The resulting mixture of reacted coal fines and reagent liquor is further processed to efficiently separate

the coal fines from the liquid fractions. The fines at this point are physically compatible with **agglomeration** and are susceptible to such processes under surprisingly moderate conditions. Generally, temperature is not a concern in the **agglomeration** process of the present invention, but, as will be discussed further, it may have significant peripheral advantages in the recycling of reagent and the preparation of a final agglomerated product.

The agglomerated coal fines of the present invention have controllable hardness qualities. Compression of the treated fines results in pellets or briquettes of various sizes, although the five-eighths (5/8) inch by one (1) inch diameter pellet has significant commercial appeal. The treated and compressed product is surprisingly resistant to water absorption and is stable over a wide temperature range.

The advantages of the present invention result from the ability to produce the desired product under conditions utilizing low energy and high reagent recovery. Typical reagent recovery is as high as ninety-nine percent (99%) and actual reagent concentration may be adjusted to affect the final product hardness. These advantages and other distinguishments of the present invention will become more apparent as the preferred embodiment is discussed below.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart diagram of the process of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A process for the **agglomeration** of coal fines and a product deriving therefrom, according to the present invention, is described herein. The coal fines from whatever source are made susceptible to compressive treatment, such that the resulting pellets or briquettes can be utilized via standard commercial applications.

Turning now to the drawing, FIG. 1 shows the steps of the process via a flow chart diagram. Generally the steps of the process of the present invention are as shown, although it is recognized that some minor variations may exist. For example, additional chemical treatment such as a washing step may be employed, as will be discussed further, and this is not represented within the steps outlined in FIG. 1.

Other variations from the process thus outlined may be made without departing from the practice of the present invention. One skilled in the art may appreciate the possibilities of combining or adding steps to the process to effectuate a particular result. The objective of the present invention is the facilitation of developing or enhancing the **agglomeration** capabilities in untreated coal fines.

The coal fines utilized in the present invention may be derived from any of the three major groups of coal products or ranks. These are the bituminous, sub-bituminous and the lignite types, all of which are usually geographically segregated. The process of the present invention is applicable to all three types, although as will be discussed, the sub-bituminous coals may require additional treatments in order to achieve commercially acceptable grades of pellets or briquettes.

The source or origin of the coals notwithstanding, the generation of coal fines through many of the standard coal applications or in the handling or transport of coal will usually result in quantities of a powder looking material with poor prospects for immediate reuse. The fines are many times relegated to settling ponds where the accumulations are kept from becoming ecological disasters by virtue of submersion under water. Periodic excavation of such ponds produces large volumes of fines that for the most part, are handled as if they were hazardous waste materials. Utilizing coal fines from such sources even as this does not present a problem for the present invention.

The criterion for the coal fines to be employed in the preferred embodiment relate largely to maximum particle size and moisture content. The particle size is important since it defines the surface area being contacted by reagent, and as between the coal particles themselves. The moisture content is a factor in determining how long the process will take to complete, the occurrence of water being an inhibiting factor in the **agglomeration** process.

Moisture content, as indicated above, has an inhibiting effect on the **agglomeration** process, and coal fines with moisture content greater than twenty-two percent (22%) have significantly reduced efficiency. Since the moisture content does not impart a favorable effect, coal fines with overall moisture content substantially less than twenty-two percent (22%) would be compatible with the process of the preferred embodiment.

Moisture content in the coal fines retards the process of the present invention. This does not represent a problem normally in that insofar as the applicant has been able to determine most of the coal fines generated have less than the preferred level of twenty-two percent (22%) moisture. Tests have been run on coal fines containing as much as thirty-two to thirty-four percent (32-34%) moisture content with satisfactory, albeit delayed results.

The particle size of the coal fines is at least initially an important consideration. The process of the present invention preferentially operates with coal fines less than two hundred (200) microns in size. The distribution of particle size within any sample of coal fines will vary over a range. This variance may reflect the difference in the degree of handling or the origin of the coal fines. The fines need only be classified as to maximum size for the purposes of the present invention through means that are well known in the art and do not represent a part of the present invention. The smaller sized coal fine particles do not detract from the process; in fact it appears that the objective of sizing the coal fines relates to a requisite amount of surface area in order to initiate the reactions of the process. Particle sizes smaller than this requisite amount, may have enhanced efficiencies in terms of speed of reaction, but such advantages do not appear to be commercially distinguishable.

Coal fines have been tested specifically as low as six (6) micron particle size range. It is known in the industry particle sizes as small as six-hundredths (0.06) microns are found, although these have not specifically been tested. It is the belief of the applicant that all practical sizes of coal fines such as those being actually generated in related industries, will be susceptible to the process of the present invention at least to the extent that the particles are sized below the two hundred (200) micron level.

During the next phase of the process, the fines are mixed with the reagent chemicals. The reagent chemistry developed for this process favors a relationship whereby the reagent is a proton donor to the reactant coal fines. Various compounds have been tested in this regard, and a number of classes appear to be compatible with the process.

The class of aromatic tertiary amines appears to be the most effective of the compounds used as reagents in the process. Various members of the aromatic tertiary amines have been tested in the process of the present invention, including quinoxaline, cinnoline, quinazoline, acridine, phenazine, phenanthroline, phenanthridine, quinoline and isoquinoline. Of these, the preferred reagent is quinoline, although, as will be explained, isoquinoline is actually more effective.

Other organic groups have been tested for effectiveness in the process with the result that cyclic nonaromatic amines have been found to function in the process as well. Specifically morpholine is quite effective in achieving the desired reactions of the process. In addition, tests have been conducted on various primary amines which have similarly been effective in achieving the same results.

Tests conducted using morpholine, piperazine, piperidine, pyrrolidine, and pyrrole have shown these cyclic nonaromatic amines to induce the **agglomeration** characteristics of the present invention. Tests conducted on various primary amines such as dipropylamine and triethylamine have also proved to be effective in the process.

The preferred compound, quinoline, is typically diluted with a selected solvent. The preferred concentration range is equivalent to two (2) mls of quinoline dissolved in eight (8) mls of solvent per ten (10) grams of coal fines. Thus the overall ratio of reagent and solvent to coal fines is 1:1 volume to weight. In terms of the handling of the coal fine and reagent slurry, this ratio seems to have some advantages. It can be seen from the nature of the process that more or less solvent may be added without impairing the basic reactions, although it may mechanically impair the completeness of the process. The ratio of reagent and solvent to coal fines may be as high as 2:1 and still be commercially attractive. Ratios higher than this would still be effective in the process but corresponding increases in equipment handling problems and wastage render these less than optimal.

Amounts less than the two (2) mls of quinoline per ten (10) grams of coal fine sample may be utilized, but the results again will impact completeness of the reaction process. It appears from analysis of the recovered products and reactants that approximately one to two percent (1-2%) of the quinoline reactant is actually consumed or lost. The lowest concentration for reacting the quinoline of the present invention with coal fines would be two-hundredths (0.02) mls per a ten (10) gram sample of coal product. Commercial feasibility at this level is unattractive since the reaction kinetics would inhibit satisfactory yields over extended periods of time. Additions greater than the two (2) mls of quinoline per ten (10) grams of coal fines would be effective but redundant in terms of maximizing the benefits of process. Since many of the aromatic and nonaromatic amines feasible for this process are quite viscous, the effects of raising concentrations much above the two (2) mls per ten (10) gram level would result in difficulty in slurrying the coal fines and reagents. As a practical limit, the usage of more than three (3) mls of quinoline would be excessive in the practice of the present invention. Adjustments in the concentration greater than 3 mls may be made if hardness of the compressed coal product is to be correspondingly increased. Further discussion of this aspect occurs within the specification. One skilled in the art would certainly appreciate the consequences of such additions and would modulate conditions to achieve the best effect possible.

The usage of isoquinoline in the present invention is more effective than the preferred quinoline. Tests have indicated that isoquinoline is four to ten percent (4-10%) more effective than quinoline. From a commercial standpoint it is difficult to acquire isoquinoline in amounts sufficient for large scale operation of the present invention. Thus, the readily available quinoline chemistry is preferred in order to achieve the stated objectives of economy.

The addition of solvent to the quinoline reagent not only has the benefit of enhancing the handling characteristics of the reagent mixture, but is believed to assist in dispersion and mixing. Additions of various solvents have observably improved the completeness of reaction between the quinoline of the preferred embodiment and the coal fines. Whether this is a function of the increased penetrability with solvent type materials or whether it relates to mechanical factors in mixing and handling, the effect is still the same in the sense that the reagents more completely interact with the reacting coal fines.

The preferred solvent is dimethylacetamide. Other solvents that have been tested and found to be effective include toluene, chloroform and carbon disulfide. The addition of solvent has the benefit of reducing the unpleasant odors associated with organic amines. In the case of the preferred reagent, quinoline, the aromatic amine odor is quite pungent and is typical of the members of its chemical family. The solvent additions for reasons not fully understood, appear to mask the amount of odor being

generated by the reactant under process conditions.

The reagent chemicals of the process share many common attributes as would be expected. They are distillable and possess similar water solubility characteristics. As will be seen, these traits are useful and can be exploited in the process of the present invention to achieve recoveries and efficiencies that have prevented useful processing of coal fines in the past.

One curious aspect of the process of the preferred embodiment is that it has been found the reaction between the aromatic tertiary amines and the coal fines proceeds more efficiently in the dark. Specifically, the exclusion of visible light results in better reaction efficiencies and the recovery of viable reactants. For the purposes of the present invention, the process may be enclosed within reaction vessels, thus eliminating the exposure to visible light; or in the alternative, it may be conducted within facilities that can be darkened for the same purpose. To date, tests conducted have indicated that nominal intrusions for inspection of process wherein small amounts of visible light or select light, such as red filtered light, do not poison or spoil the process and the benefits normally achieved. The light sensitivity is related to the quinoline and isoquinoline products, since tests performed on other reactants have not indicated this same sensitivity.

The actual **agglomeration** process may be regulated by the usage of low weight alcohols. In particular, ethanol has been used successfully to regulate the speed of the agglomerating coal fines whether they are being vacuum dried or pelletized. The spray washing of coal fines with ethanol slows down the **agglomeration** process, thus allowing the development of a compact and cosmetically acceptable coal product. The actual adjustment required may depend in part on the origin of the coal fines, the particular reagent and solvent combination, and the conditions of the drying process. Given the volatile nature of the ethanol, it is not found in the resulting coal product in any significant quantity. The purging or washing of coal fines with alcohol is merely a control feature for improving the cosmetics and quality of the coal pellet, and as such does not represent a critical factor in the practice of the process.

Turning now to the post-reaction aspects of the process, the coal fines reacted with the appropriate organic amine are removed from the reaction slurry. The coal fines may be allowed to settle in a sedimentation vessel and then are drawn off for subsequent drying and compressing. The aspects of sedimentation are well known in the art and are a matter of engineering selection as to the deployment of size and type of vessels, withdrawal apparatus, and other functional attributes.

The settled coal fines, once collected, can be dried successfully by at least two processes. The first is vacuum filtration wherein the collected coal fines are presented to vacuum drying apparatus such as rotating vacuum filters. The reaction liquors are extracted from the collected coal fines and are returnable to the process.

The collected coal fines may also be dried by means of pelletizing. It has been found that by pelletizing the product of the present process under conditions of moderate temperatures, that flash volatilization of the reagent liquor takes place, leaving a pressed, dry coal fine product. The vaporized reagent liquor may be collected and returned back to the process.

Neither method of post-reaction processing should be viewed as a limitation on the process itself. The mechanical treatments involved can be scaled to compatibly receive the output of the process so as to provide a virtually continuous treatment system.

EXAMPLE I

A one hundred (100) gram of coal fines is sieved for particle size under two hundred (200) microns. The

sieved fines are then added to a reagent comprising twenty (20) mls of commercial grade quinoline dissolved in eight (80) mls of dimethylacetamide. The slurry is mixed for three (3) minutes and is vacuumed filtered to remove any liquid portions as filtrate. The filter cake is allowed to air dry and results in a compact coal agglomerate product.

EXAMPLE II

A one hundred (100) gram sample of coal is treated as above, except the slurry mixture is added directly to a pelletizing device. While maintaining the temperature of a pelletizer at one hundred degrees Centigrade (100.degree. C.), the slurry is compressed forming a pellet with an apparent density between 1.0 grams per cubic centimeter (cm.sup.3) and 1.5 grams per cm.sup.3. The resulting pellet has the appearance of a solid coal product and resists crumbling and dusting.

EXAMPLE III

Coal fines were sieved for particle sizes below one hundred fifty (150) microns. The fines thus collected were added to a reagent comprising ninety-eight percent (98%) m-xylene fused with two percent (2%) pyridine. The slurry is then agitated for one-half (1/2) minute, and then a subsequent addition of two percent (2%) by volume of toluene is added. Upon further agitation for approximately two (2) minutes, the solution is then vacuumed filtered and the filter cake is allowed to air dry. The cake produces a satisfactory agglomerate giving the appearance of a coal solid.

As can be seen from the foregoing, various methods for practicing the present invention are possible. The desired end product of the process, however, is a compressed coal product giving the appearance of a coal solid, with high integrity that is resistant to crumbling or dusting. In addition, beneficial characteristics such as low moisture content and resistance to moisture pick-up are results of the process of the present invention.

Specific testing of the pellets produced from the present invention have shown that the stability of the pellets is very high, exceeding industry expectations in most cases. Testing under extreme conditions has shown that the integrity of the pellet is maintained during exposures between minus five degrees centigrade (-5.degree. C.) and up to seventy degree centigrade (70.degree. C.) for days at a time. In addition the pellet integrity was maintained under the same conditions when the pellet was totally immersed in water. Testing of the immersed pellets range from one (1) hour of immersion to three (3) days or more with no loss of pellet integrity.

The hardness of the compressed product from the process of the present invention can be measured via the Hardgrove Grindability Index. The Hardgrove Index of the vacuumed filtered product ranged from 77.0 for pellets formed under twenty-three (23) inches Hg vacuum to 83.0 on the Hardgrove scale under conditions of twenty-seven (27) inches Hg vacuum. Surprisingly, the hardness of the final coal product can be adjusted by modifying the reaction conditions. Increasing the ratio of the preferred reagent quinoline to solvent will result in increasing the hardness of the pellets formed by the present process.

Agglomerated coal fines were tested for hardness under varying concentrations of reagents. At a concentration of approximately sixty percent (60%) quinoline, or six (6) mls per ten (10) grams of coal fines, a maximum hardness of product was achieved which is substantially greater than virgin coal. While this concentration of the preferred reagent is greater than the range discussed before, it is a reflection of the range of characteristics that can be developed by the process. The consequences of agglomerated coal fine pellets with hardnesses greater than coal itself mainly impacts in transport and handling.

The characteristic of water resistance of the pellets produced from this process may come about as a result of the nature of the reaction between the chemistry in the coal fines. It is believed that the final agglomerated product is a more saturated organic product than the starting material and the result of this hydrogen loading is to resist infiltration of the coal product by water. The hydrophobic characteristics of the finished product have significant commercial interest since transport of moisture laden coals adds to the cost of transport and results in difficulties especially in cold weather. The tendency for coal products to freeze together can deter the usage of coal in northern climates where the demand for cheap energy resources is most acute. In addition, the infiltration of water into coal products lowers the net BTU (British Thermal Unit) value of combustion. Eliminating or reducing the infiltration of water is a feature of the present invention that directly affects the economics and feasibility of utilizing agglomerated coal fines.

The usage of the present process on sub-bituminous coal, or "western coal", is possible by slight modification. It has been found that the iron concentration, in the form of hematite, plays at least a modest role in the **agglomeration** process. While hematite is naturally occurring in coals from other sources, the western coal contains little and needs to have adjustments in the hematite concentration in order to achieve maximum results under the process of the present invention.

In order to optimize the conditions for pelletizing, it has been found that additions of one percent (1%) hematite by weight results in pellets of high quality. Additions greater than this amount will still result in good quality pellets, however, the additional increase in ash content is considered undesirable. Correspondingly, less than one percent (1%) hematite additions to western coal fines reduces the pellet quality proportional. One skilled in the art could modulate additions above and below the optimal one percent (1%) range to achieve an engineered result. From a general standpoint, it would be undesirable in any event to increase the hematite concentration above five percent (5%) since the utility of the resulting pellet would be reduced to the point of making it impractical for most routes of consumption.

The inclusion of hematite in the western coal fines has been tested for any potential effects on Hardgrove Index. Testing has indicated that additions do not contribute in any significant way to increases in the Hardgrove Index, the hematite concentration apparently assisting in the **agglomeration** process itself by adjusting acid/base ratios.

The usage of a pelletizer in the present process is an advantage over the vacuum or air drying of agglomerated coal fines. The pelletizing apparatus is typically constructed to operate at a temperature of approximately one hundred degrees Centigrade (100.degree. C.) and under thirty (30) inches Hg pressure. The heat in the pelletizer head, along with the action of the pelletizing device itself, is sufficient to drive the reagent and solvent portion from the pelletizing apparatus. The volatilization of the preferred quinoline and dimethylacetamide can be controllably recovered by condensation techniques. Thus, the loss of valuable chemistry is reduced while providing a means for expeditious drying of the coal fine product.

The recovery of reagent and solvent from the pelletizer has been demonstrated to be as high as ninety-nine percent (99%). It appears that from the work done so far that the pelletizer recoveries are expected to be higher than that which may be achieved by a vacuum filtration. Since the capacity of the pelletizing operation can be adjusted to handle the volume of a continuous system, it represents the most efficient means of practicing the art of the present invention.

The quality of the pellet produced as a result of the present process can be affected by the exposure to visible light, by the water content, and by the hardness engineered for the pellet. Commercial acceptance of pelletized coal fines is primarily founded on the usage of these as a combustible material. Feedstocks for boilers and furnaces would find the pellet form most attractive, easily handled and transportable.

With these factors in mind, it can be seen that the pellets of the present invention can be developed specifically for the application to achieve the desired qualities for usage in the particular application.

It can be appreciated by one skilled in the art that various and modifications on the preferred embodiment of the present invention can be practiced without straying from the spirit and scope of the present invention. The examples and preferences expressed are meant to be illustrative of the practice of the process and are not expressed as limitations thereof.

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